

## SPECTROSCOPY OF HIGH TEMPERATURE MOLECULES

Leo Brewer

Inorganic Materials Research Division of  
Lawrence Radiation Laboratory and Department of Chemistry  
University of California, Berkeley, California 94720

High temperature furnaces, flasher, arcs, and similar sources of high excitation are the conventional sources of spectra of high temperature molecules. However, spectra from such sources are often difficult to resolve because of the high electronic, vibrational, and rotational excitation resulting in extensive overlapping of spectral bands. Excitation of impurity molecules increases the complications due to overlapping.

It is important to obtain complete analyses of the band systems of high temperature molecules to establish the spectroscopic constants needed for calculation of the high temperature thermodynamic properties. In particular the establishment of the degeneracies and energies of all low lying electronic states is very important.

The failure of conventional methods to produce the needed information has stimulated a variety of new approaches. This paper will discuss the potential advantages and handicaps of the new methods and will suggest other approaches.

A rather widely applied method in the last few years involves the entrapment of high temperature molecules in a rare gas or other inert matrices at liquid hydrogen or helium temperatures. This method offers a simplification of the analysis of the spectrum in that one would expect the entrapped molecules to be in their lowest electronic and vibrational states. The absorption spectrum of  $S_2$  in a matrix is found to consist of a single progression arising from the  $v'' = 0$  level of the ground electronic state. When there are almost degenerate electronic states around the ground state energy, it is possible that interactions with the matrix might invert their order and thus indicate the incorrect gas ground state. A more severe disadvantage of matrix absorption spectra is the lack of sharpness and detail such that electronic spectra can not be unambiguously

identified without knowledge of the gas spectra. A most serious disadvantage of matrix absorption spectra is that information is not obtained for low lying electronic states.

Another fruitful approach to simpler high temperature spectra is through use of molecular beams from a Knudsen cell or some other high temperature source of vapor. During the typical transit times of  $10^{-4}$  to  $10^{-5}$  seconds, one would expect the excited electronic states to decay to the lowest state of each multiplicity for light molecules and to the ground state for heavier molecules for which the spin change prohibition is not rigid. Thus the molecular beam should provide simpler spectra. A variety of spectral measurements can be made on a beam. For example, electric-resonance and magnetic deflection experiments by Klumperman and his coworkers have been used to establish an  $O^+$  ground electronic state for SrO and BaO. Also for triatomic and more complicated molecules, they have shown that electric-deflection experiments can be used to determine the symmetry of the molecules. The combination of a Stern-Jerlach experiment with a mass spectrometer detector offers to be a useful way of distinguishing singlet from triplet ground states or of determining the splitting of triplet ground states of heavier molecules. For example, Scarcy and Hoesli have used this method to confirm that the 1 sublevel of the  $^3\Sigma$  ground state of  $Te_2$  lies so far above the  $O^+$  sublevel that the beam of  $Te_2$  shows no deflection. Optical absorption or fluorescent experiments may also be carried out on molecular beams. In this manner Brewer and Welch have established the ground state of LaO and Brewer and Green have shown that the lowest singlet and triplet states of SrF are virtually degenerate since both states persist in a molecular beam for longer than  $10^{-4}$  sec. Although these various applications of molecular beams have been useful in establishing the very lowest electronic states, they do not provide information about the low-lying excited states which are important with respect to their contribution to the high temperature partition function since these states will have usually decayed in the

transit time of the beam.

There is a possibility of eliminating the limitation of absorption spectra of molecular beams and matrices through use of fluorescent spectra. By exciting to very high electronic states, one can observe cascading through the lower electronic states. The matrix spectra offer the advantage of relatively rapid vibrational deactivation and the fluorescent spectra often consist of simple progressions arising from the  $v' = 0$  level of the upper electronic state. The matrix method offers the other advantage of enhancement of forbidden transitions which could allow the fixing of the energies of singlet and triplet states relative to one another. Meyer, Phillips, and Smith have applied this method recently to  $\text{SO}_2$ .

A new method has been suggested that might be able to provide direct information about the energies of all of the low-lying electronic states of a molecule. For example, the first excited  $\frac{1}{2}^+$  state of  $\text{CaO}$  is perturbed by six different low-lying states or sublevels. From the perturbations observed for  $\text{Ca}^{16}\text{O}$ , the vibrational and rotational constants of these states can be established, but their energies are not known. A similar analysis of the perturbations for  $\text{Ca}^{18}\text{O}$  may allow fixing of the energies of each of the states from the isotope shift.

The application and potential future applications of the above methods will be discussed. This work has been supported by the Research Division of the Atomic Energy Commission.